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Influence of ^4He Impurities on Nuclear Spin Relaxation in Solid ^3He *

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The NMR properties of solid ^3He , mainly the ratio of the heat capacities of exchange and Zeeman energies and the exchange-lattice relaxation times are very sensitive to the presence of ^4He impurities, while the transverse relaxation time T_2 does not depend on the impurity concentration when the latter remains small. These properties can be explained in two different ways. (1) We assume an enhancement of exchange interactions around ^4He impurities. We derive the consequences of such an assumption and compare them with experimental results. For two molar volumes in the bcc phase, the locally enhanced exchange is equal to approximately $7J$, with J being the exchange in pure ^3He . (2) Guyer and Zane introduce a mass fluctuation wave to explain the excess of heat capacity and the dependence of the longitudinal relaxation time with concentration. Both these models give rise to a four-energy bath system. As in the bcc phase, the exchange-lattice relaxation time in the hcp phase decreases when x increases at low enough ^4He concentrations. For $V = 18.48 \text{ cm}^3$ we deduce the coefficient for translational diffusion from high-temperature experiments with the help of Torrey's theory for spin-lattice relaxation.

1. INTRODUCTION

We report results of NMR experiments on samples of solid ^3He containing impurities of ^4He . Our results are consistent with two different points of view.

(1) At first we develop a theoretical model previously proposed¹ to analyze NMR experiments in bcc solid ^3He containing low atomic concentrations, x , of ^4He impurities. The spin-system energy in solid ^3He is generally supposed to be split into two independent reservoirs more or less tightly bound to one another and to the lattice.^{2,3} This model is quite adequate to study pure solid ^3He but cannot explain the experimentally observed modifications of the NMR properties in presence of ^4He impurities.⁴ We suppose this inadequacy to be due to an increase of the exchange parameter J in the neighborhood of ^4He atoms in impure solid ^3He . Furthermore, we assume that these enhanced exchange interactions J_E can be described by a local spin temperature.

(2) We alternately consider a tunneling model recently proposed by Guyer and Zane⁵ which explains the experimental data without the help of enhanced exchange interactions.

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According to these models, we analyze both spin-lattice and transverse relaxation. The consequences for the evolution of the different relaxation times and heat capacities with temperature and concentration of impurities are very similar in both cases. Since microscopic theoretical calculations^{6,7} failed so far to account for the variation of the exchange parameter in the neighborhood of ^4He impurities, the problem remains of finding experimental evidence to prove the validity of one or the other assumption.

We report pulsed NMR measurements of spin-lattice and transverse relaxation times, and also of the ratio R of heat capacities of exchange to Zeeman baths. In the bcc phase, experiments are made at a frequency $\omega/2\pi = 2.19$ MHz and x varies between 5×10^{-5} and 2.8×10^{-3} . In order to measure exchange contribution to spin-lattice relaxation, the Zeeman relaxation due to atomic diffusion is suppressed by working at sufficiently low temperature. We compare our results with those of some authors.

In the bcc phase, in our range of concentration, the exchange-lattice relaxation time is a decreasing function of x ; in the hcp phase the range of concentration is larger and goes up to 8.7×10^{-3} . Our data seem to indicate that the exchange-lattice relaxation time ceases to be a monotonic decreasing function of x for large x .

2. THEORETICAL MODELS

2.1. Enhanced Exchange

Let us recall the assumptions of our first model.¹ We consider a crystal of bcc solid ^3He where one ^3He is replaced by ^4He . We expect a distortion of the lattice near this impurity,^{8,9} the ^3He atoms being displaced towards the substitutional ^4He . Let us assume that this distortion is important only for the first shell of eight ^3He atoms, A , surrounding ^4He . There are 26 ^3He atoms, B , nearest neighbors of atoms A , and 56 pairs of first-neighbor atoms AB .

We assume the exchange interaction for these 56 pairs AB have a common averaged value J_E enhanced with respect to exchange interactions J in pure ^3He or far from ^4He . We emphasize the fact that, as in pure ^3He , we assume no exchange interaction between two ^3He atoms which are not nearest neighbors of one another. In the bcc phase, two ^3He atoms first neighbors of ^4He are never first neighbors of one another.

The total exchange Hamiltonian $\hbar\mathcal{H}_{\text{ex}}$ is thus split in three parts:

$$\mathcal{H}_{\text{ex}} = \sum_{i < j} J_{ij} \mathbf{I}_i \cdot \mathbf{I}_j = \mathcal{H}_E + \mathcal{H}_N + \mathcal{H}'_N \quad (1)$$

$\mathcal{H}_E$ includes the enhanced interactions J_E between pairs AB which surround each ^4He impurity. $\mathcal{H}'_N$ includes the interactions J between pairs BC , C which undergo only normal interactions and thus are at least second neighbors of an atom A . $\mathcal{H}_N$ includes the remaining interactions J between pairs CC .

We note that, so defined, $\mathcal{H}_E$ and $\mathcal{H}_N$ commute with each other, but neither one commutes with $\mathcal{H}'_N$.

The unperturbed Hamiltonian $\hbar\mathcal{H}_0$ in a dc magnetic field is chosen as:

$$\mathcal{H}_0 = \mathcal{H}_Z + \mathcal{H}_E + \mathcal{H}_N \quad (2)$$

where $\hbar\mathcal{H}_Z$ is the Zeeman Hamiltonian. The perturbation $\mathcal{H}_P$ is then the sum of $\mathcal{H}'_N$ and of the dipolar interaction $\mathcal{H}_d$, which is much smaller than $\mathcal{H}'_N$. The system is described by the density matrix:

$$\sigma \propto 1 - \beta_Z \mathcal{H}_Z - \beta_N \mathcal{H}_N - \beta_E \mathcal{H}_E \quad (3)$$

where $\beta_Z, \beta_N, \beta_E$ are the inverse temperatures of the different baths.

2.1.1. Spin-Lattice Relaxation

In the same way as for pure ^3He ^{8,10} we investigate the time dependence of the inverse temperature of the Zeeman and exchange baths by using the master equation for the density matrix in the interaction representation.¹¹ The calculation yields:

$$-\dot{\beta}_Z = W_{ZE}(\beta_Z - \beta_E) + W_{ZN}(\beta_Z - \beta_N) \quad (4)$$

$$-\dot{\beta}_N = W_{NE}(\beta_N - \beta_E) + \frac{\text{tr}\{\mathcal{H}_Z^2\}}{\text{tr}\{\mathcal{H}_N^2\}} W_{ZN}(\beta_N - \beta_Z) + W_{NL}(\beta_N - \beta_L) \quad (5)$$

$$-\dot{\beta}_E = \frac{\text{tr}\{\mathcal{H}_N^2\}}{\text{tr}\{\mathcal{H}_E^2\}} W_{NE}(\beta_E - \beta_N) + \frac{\text{tr}\{\mathcal{H}_Z^2\}}{\text{tr}\{\mathcal{H}_E^2\}} W_{ZE}(\beta_E - \beta_Z) + W_{EL}(\beta_E - \beta_L) \quad (6)$$

where β_L is the inverse temperature of the lattice.

$$W_{NE} = \left[\int_0^\infty d\tau \text{tr} \{ [\mathcal{H}_N, \mathcal{H}_P] U(-\tau) [\mathcal{H}_E, \mathcal{H}_P] U(\tau) \} \right] / \text{tr} \{ \mathcal{H}_N^2 \} \quad (7)$$

$$W_{ZN} = \left[\int_0^\infty d\tau \text{tr} \{ [\mathcal{H}_N, \mathcal{H}_P] U(-\tau) [\mathcal{H}_Z, \mathcal{H}_d] U(\tau) \} \right] / \text{tr} \{ \mathcal{H}_Z^2 \} \quad (8)$$

with $U(t) = \exp(i\mathcal{H}_0 t)$ and a similar equation for W_{ZE} where N is replaced by E. These equations have also been obtained in Ref. 12 by introducing the lattice parameters in the master equation from the very beginning.

Some of the different relaxation rates W we have just defined depend on the ^4He concentration in the sample. We show in Appendix I that W_{NE} is proportional to x ; the same holds true for W_{ZE} , while W_{EL} and W_{NL} are expected to be independent of x , in the limit of small ^4He concentration. A quantity of special interest is W_{NE} which describes the energy transfer between the two exchange baths. If W_{NE} is large compared to the other W , the main part of the spin energy will be transferred to the lattice through that exchange bath whose relaxation rate with the lattice is the larger. If W_{NE} is small compared to the other W , there will be two independent relaxation paths to transfer the Zeeman energy to the lattice.

Let us now evaluate W_{NE} by expanding the exponentials in the trace and assuming $\mathcal{H}_d$ to be small with respect to $\mathcal{H}'_N$, we then replace the integrand by a Gaussian function of τ , the curvature at origin of which can be calculated.

This "Gaussian assumption" often made in the theories of magnetic resonance^{13,14} leads to the following result:

$$W_{NE} = -\sqrt{\frac{\pi}{2}} \frac{\text{tr} \{[\mathcal{H}_E, \mathcal{H}'_N]^2\}}{\text{tr} \{\mathcal{H}_N^2\}} \sqrt{\frac{-\text{tr} [\mathcal{H}_E, \mathcal{H}'_N]^2}{\text{tr} \{[(\mathcal{H}_E + \mathcal{H}_N), [\mathcal{H}_E, \mathcal{H}'_N]]^2\}}} \quad (9)$$

With this assumption W_{NE} appears to be proportional to J_E and also to x . The proportionality to x is already established in a more general fashion.

2.1.2. Transverse Relaxation¹

In a similar way, we investigate the time dependence of the precessing transverse magnetization. As in pure ^3He ⁸ it can be shown that the transverse relaxation is described by a single exponential with a characteristic time T_2 ; its adiabatic contribution T'_2 which is predominant for high enough magnetic field is given by

$$1/T'_2 = \frac{1}{2} \int_{-\infty}^{+\infty} G_\omega(\tau) d\tau \quad (10)$$

where $G_\omega(\tau)$ is the correlation function for the modulation of the dipolar field by exchange. It can be shown that the correlation function splits into three parts where the modulation is due respectively to the normal exchange, the enhanced exchange, and a combination of the two exchange mechanisms [Appendix II]. The magnitude of the relative contributions of these three modulations to the linewidth is determined by the number of bonds where the exchange is modified, and although one might think the larger frequencies would be more efficient for the narrowing, the most important contribution is still that of the unperturbed exchange, the correction due to the displacement of the other frequencies being roughly proportional to this displacement. We evaluate this correction by assuming that the three functions are Gaussian with characteristic frequencies ω_N , ω_E , and ω_P ($\omega_E > \omega_P > \omega_N$). Calculating the lattice sums in the case where the sample is a powder, we get

$$1/T'_2 = [1/(T'_2)_{\text{pure}}] \{1 - x[53.46 - 42.33(\omega_N/\omega_P) - 9.13(\omega_N/\omega_E)]\} \quad (11)$$

with

$$(1/T'_2)_{\text{pure}} = \sqrt{\pi/2} (M_2/\omega_N) \quad (12)$$

M_2 is the second moment for pure ^3He . If the exchange enhancement is large ($J_E \gg J$), i.e., ω_N is small with respect to both ω_E and ω_P :

$$1/T'_2 \simeq (1/T'_2)_{\text{pure}} \{1 - 53.46x\} \quad (13)$$

We note that for $J_E = J$ the x coefficient in (11) is not zero but -2 due to the ^4He atoms without magnetic moment distributed in the crystal. We also note that the concentration dependence shown by (13) is very different from that of the fourth moment of the resonance line, which is of the form

$$M_4 = (M_4)_{\text{pure}} \{1 + Ax(J_E/J)^2\} \quad (14)$$

when $J_E \gg J$.

Let us mention that (11) depends on the Gaussian assumption only through the precise definition of the characteristic frequencies ω_N , ω_P , and ω_E , but not through the numerical coefficients, which are directly related to lattice sums.

Generally speaking and before we analyze our experimental results, we must emphasize that the model we just described is only valid in the limit of small impurity concentration and large exchange enhancement.

2.1.3. Susceptibility

The susceptibility can be obtained from the partition function Z for the system by :

$$\chi = \frac{\partial^2}{\partial H^2} [k_B T \log Z] \quad (15)$$

with

$$Z = \text{trace} \{ \exp(-\mathcal{H}_0/k_B T) \} \quad (16)$$

We are here concerned with high temperatures, well above the alignment point. By expanding the partition function and then χ in powers of $(1/T)$ up to the T^{-2} terms, we get

$$\chi = \frac{(\hbar\gamma)^2 N}{4k_B T} \left[1 - x - 2 \left\{ \frac{J(1 - 54x) + 14J_E x}{k_B T} \right\} \right] \propto \frac{1}{T} - \frac{\theta}{T^2} \quad (17)$$

The Weiss constant θ is then :

$$\theta = 2 \frac{J(1 - 54x) + 14J_E x}{(1 - x)k_B}$$

instead of $\theta_0 = 2J/k_B$ for pure ^3He .

Then $\theta/\theta_0 = 1 + x[14(J_E/J) - 53]$, which gives for $V = 20.06 \text{ cm}^3$, using the J_E and J values we evaluate in the next section, $\theta/\theta_0 = 1 + 55x$. This modification of the Weiss temperature due to impurities cannot be seen experimentally in the limit of small concentrations where the model is expected to be valid.¹⁵⁻¹⁸

2.2. Mass Fluctuation Waves

Let us now consider another model recently proposed by Guyer and Zane (GZ).^{5,19} Following GZ, the motion of ^4He particles leads to a mass fluctuation wave, to which is associated an energy bath. They derive the dispersion relation for these new excitations, which in the $k \rightarrow 0$ limit is

$$\hbar\omega(k) = \Delta\epsilon_4 + Z \frac{J'}{2} (ka)^2 \quad (18)$$

where $\Delta\epsilon_4$ is a finite energy shift, Z is the number of near neighbors, a is the near neighbor distance, and the crystal has been assumed to have simple cubic structure. J' is of the order of the tunneling frequency for a substitutional ^4He atom embedded in solid ^3He . J' is assumed to be of the order of J . This dispersion relation remains valid for a bcc lattice in the $k \rightarrow 0$ limit.

The specific heat of the ^4He system is assumed to be that of a gas of excitations for which the dispersion relation is given by (18) for any wavevector k up to the zone boundary. This gives for a bcc lattice:

$$C_4/N = 35xZ^2k_B \left(\frac{\hbar J'}{k_B T} \right)^2 \quad (19)$$

Using the values of J' of the order of J for our experiments, it can be easily shown that these excitations are never in a degenerate state at the temperature where we work.

The experimentally observed long relaxation time is then found to be

$$\frac{1}{T_1} = \frac{1}{T_1^0} \left\{ x / \left[x + \frac{10^{-3}}{9} \left(\frac{\omega}{J'} \right)^2 + \frac{10^{-3}}{3} \left(\frac{J}{J'} \right)^2 \right] \right\} \quad (20)$$

for a bcc lattice with our definition of J .

For this lattice the relaxation rate of the intrinsic process is given by

$$\frac{1}{T_1^0} \sim 33 \left(\frac{\delta M}{M} \right)^2 \frac{k_B T}{\hbar} \left(\frac{T}{\theta_D} \right)^6 \quad (21)$$

where θ_D is the Debye temperature of the solid and $(\delta M/M)$ is the mass fluctuation. This gives $T_1^0 \sim 10^{-2}$ sec at $V = 20.0 \text{ cm}^3$ and $T \sim 0.5 \text{ K}$. In our calculations using this model we took $\delta M/M = \frac{1}{3}$, but, as in the case of phonon scattering by static impurities, it would be better to consider both mass defect and the distortion of the crystal around the impurity,²⁰ which change the phonon spectrum. According to Grüneisen approximation, the coefficient $(\delta M/M)^2$ in (21) would be replaced by $[(\delta M/M)^2 + 4\gamma^2(\delta V/V)^2]$, where γ is the Grüneisen constant and $\delta V/V$ is the relative modification of the atomic volume due to the introduction of a substitutional impurity in the lattice. This last coefficient is directly related to the measurements of thermal conductivity in the solid.²¹

Another point of interest is the coupling between the ^4He and the ^3He baths. The characteristic rate is:

$$\frac{1}{\tau_{34}} \sim ZJ'x \quad (22)$$

which is much faster than T_1^{-1} .

Although the origin of the new energy bath is entirely different in the two models, the expected experimental observations are very similar. The topology of the different energy baths is the same, but there is no direct Zeeman, ^4He bath relaxation in the case of mass fluctuation waves corresponding to W_{ZE} of the first model, i.e., $W_{ZE} = 0$. The coupling between the new bath and the ^3He bath is proportional to the characteristic frequency of this new bath and to the concentration. The coupling between the new bath and the lattice is stronger than the one between the ^3He bath and the lattice.

A few other points should be mentioned:

2.2.1. Transverse Relaxation Time

Let us study the influence of these mass fluctuation waves on the transverse relaxation time. In this model, T_2 is the consequence of the modulation of the dipolar field by both exchange and mass waves.

As far as NMR is concerned, ^4He is an analog of a vacancy. For the sake of simplicity, and only when considering NMR properties, we describe this motion in the random-walk manner of Torrey.^{30,31} The characteristic frequency of the exchange modulation is ω_N , of the order of J . The characteristic jumping frequency for an arbitrary ^3He atom is proportional to the jumping frequency for a ^3He first neighbor of a ^4He impurity, i.e., J' times the probability of this ^3He to be first neighbor of a ^4He , i.e., Zx ; thus we get $ZJ'x$. As J' is of the order of J , $xZJ' \ll J$, and spin exchange will consequently be more efficient than ^4He hopping to narrow the NMR line. If we want to include both effects, we can use (10) and define the correlation function $G_\omega(\tau)$ as a product of two correlation functions appropriate, one for hopping, the other one for spin exchange. This is a procedure which was already used by Hartmann³⁶ and in Ref. 2. In order to fit Torrey's theory³¹ we can write, in a phenomenological way,

$$G_\omega(\tau) = M_2 \exp\left(-\frac{1}{2}\omega_N^2\tau^2\right)e^{-j|\tau|}$$

where

$$j = 2xZJ' / 3 \int_0^\infty J_{\frac{3}{2}}^2(kx) \frac{dx}{x - \sin x}$$

The parameter k , which is defined later by means of (45) ($c \simeq 1$), is equal to 0.76293 in the bcc phase,³¹ leading to

$$j = 8.37xJ'$$

In the limit $j \simeq xZJ' \ll \omega_N$, Eq. (10) leads to an adiabatic line-width given by:

$$\frac{1}{T_2} = \left(\frac{1}{T_2'}\right)_{\text{pure}} \left\{ 1 - \sqrt{\frac{2}{\pi}} \frac{j}{\omega_N} + \dots \right\} \quad (23)$$

Since $\omega_N = 2.387J$, this last equation can be written as

$$\frac{1}{T_2} = \left(\frac{1}{T_2'}\right)_{\text{pure}} \left\{ 1 - 2.8x \frac{J'}{J} \right\} \quad (24)$$

In contradistinction to (13), the ratio J'/J now enters the x coefficient in the above equation. Since J' is not very different from J , T_2' will be very little sensitive to x . A more detailed discussion of this point will be given in Ref. 22.

2.2.2. Mass Fluctuation Waves Lifetime

The description of the ^4He impurities by mass fluctuation waves cannot be used at any temperature. To test its validity, we must check that the lifetime of the mass fluctuation waves is indeed longer than the inverse width $1/J'$ of the

corresponding band. This is done by A. F. Andreev and I. M. Lifshitz,¹⁹ who neglect the interactions between the waves and find that the defects should be considered as localized when

$$T < \theta_D \left(\frac{J'}{\Omega_D} \right)^{1/9} \quad (25)$$

where Ω_D is the Debye frequency. For $V = 20.06 \text{ cm}^3$, $\theta_D = 29.3 \text{ K}$, and using the value of J' we determine in the next section we get $T < 6 \text{ K}$, i.e., the assumption of mass fluctuation waves is always valid to describe ^4He impurities in solid ^3He at this molar volume. It is worth pointing out³⁷ that a mass fluctuation wave with a dispersion relation such as the one we gave in Eq. (18) is bound to have a very long lifetime at 0 K (forgetting phase separation for the moment) because it cannot possibly slow down by emitting either one or even several phonons and satisfy both energy and momentum conservation.

3. EXPERIMENT

In this section, we calculate the experimentally observed relaxation times with the assumption of enhanced exchange. This can be easily related to the case of mass fluctuations, for the topology of the energy baths is the same in the two cases. We give in the following table the qualitative correspondence for the two models:

Enhanced exchange	Mass fluctuation waves
J	J
J_E	J'
W_{NE}	$1/\tau_{34}$
W_{EL}	$1/T_1^0$
W_{ZE}	0
r_3	$1/T_1$

Our samples are prepared by the blocked-capillary method and the molar volume is deduced from the starting pressure. In order to check this procedure we work at pressures such that we cross the transition line between bcc and hcp phases when cooling the solid. In the transition temperature range both phases coexist, and we then observe nonexponential free-induction decays and spin-lattice relaxation. By comparison with thermodynamic measurements of the phase-transition line²³ we obtain for the molar volume two limits separated by less than 0.05 cm^3 which enclose the value we deduce from the starting pressure.

3.1. Experimental Procedure

We use radiofrequency pulses produced by a blocked oscillator and perform three kinds of experiments.

- (1) Transverse relaxation times are measured by a spin-echo technique.

(2) To obtain spin-lattice relaxation times, we let the spin system reach its equilibrium and then apply a pair of pulses of angles $\theta \sim 90^\circ$ separated by a time interval t . After each pulse we observe the free precession signal of height proportional to the total magnetization. At low enough temperature, these experiments also yield the ratio R of heat capacities of exchange to Zeeman baths.

(3) Pulse train experiments are performed by letting the spin system reach equilibrium and then applying a long train of θ degree pulses separated by a time interval τ until the system reaches a steady state. This gives information on both spin-lattice relaxation times and R .

We need to solve the equations of evolution of the inverse temperatures to obtain the time dependence of the magnetization of the sample. By solving the system of equations (4), (5), and (6), three characteristic rates r_1 , r_2 , and r_3 appear. Then β_Z , β_N , and β_E are linear combinations of three exponentials of exponents $r_1 t$, $r_2 t$, and $r_3 t$. It is not possible to get the algebraic solutions for r_1 , r_2 , and r_3 in the general case. We thus solve according to the relative values of W_{NE} compared to the other W . We obtain the following results.

(A) If $W_{NE} \gg (W_{ZE}, W_{ZN}) \gg (W_{EL}, W_{NL})$ one finds

$$r_1 \simeq -W_{NE} \left\{ 1 + \frac{\text{tr} \{ \mathcal{H}_N^2 \}}{\text{tr} \{ \mathcal{H}_E^2 \}} \right\} \quad (26)$$

$$r_2 = -\frac{(W_{ZE} + W_{ZN})(\text{tr} \{ \mathcal{H}_Z^2 \} + \text{tr} \{ \mathcal{H}_N^2 \} + \text{tr} \{ \mathcal{H}_E^2 \})}{\text{tr} \{ \mathcal{H}_N^2 \} + \text{tr} \{ \mathcal{H}_E^2 \}} \quad (27)$$

$$r_3 = -\frac{W_{EL} \text{tr} \{ \mathcal{H}_E^2 \} + W_{NL} \text{tr} \{ \mathcal{H}_N^2 \}}{\text{tr} \{ \mathcal{H}_Z^2 \} + \text{tr} \{ \mathcal{H}_E^2 \} + \text{tr} \{ \mathcal{H}_N^2 \}} \quad (28)$$

These assumptions are satisfied in high-field experiments at low temperatures.

(B) On the other hand, when $(W_{NE}, W_{EL}, W_{NL}) \ll (W_{ZE}, W_{ZN})$, two of the roots depend only on W_{ZE} and W_{ZN} . The third root r_3 is still given by (27). These assumptions can be satisfied in low-field experiments at low temperatures.

Two of the various relaxation rates we define above, W_{ZN} and W_{NL} , are known for $x = 0$, i.e., in the case of pure solid ^3He . W_{ZN} is temperature independent, while W_{NL} is strongly temperature dependent.^{12,24,4} W_{ZE} and W_{EL} are due to the same physical mechanisms as W_{ZN} and W_{NL} ; this appears in (8) for the Zeeman exchange relaxation rate. So we expect the same temperature dependence for W_{EL} and W_{NL} . In GZ model W_{NL} and $1/T_1^0$ also have the same temperature dependence.

We point out that we always find the same small relaxation rate r_3 whether W_{NE} is large or small with respect to the other W . As for small x , W_{NL} and W_{EL} do not depend on x , the x dependence of r_3 is given by the variation of the heat capacities arising in (28). This yields the result:

$$r_3 = -\frac{x[W_{EL} - \frac{54}{14}W_{NL}(J/J_E)^2] + (J/J_E)^2(W_{NL}/14)}{x\{1 - \frac{54}{14}(J/J_E)^2 - \frac{1}{42}(\omega/J_E)^2\} + \frac{1}{14}(J/J_E)^2 + \frac{1}{42}(\omega/J_E)^2} \quad (29)$$

which reduces, if $J_E \gg J$, to :

$$r_3 \simeq -\frac{xW_{EL} + \frac{1}{14}(J/J_E)^2 W_{NL}}{x + (J/J_E)^2 \frac{1}{14} + \frac{1}{42}(\omega/J_E)^2} \quad (30)$$

This is to be compared with Eq. (20) of the GZ model, where W_{NL} is neglected. When we apply a pair of pulses of angle θ , the value of β_Z after the second pulse is given by :

$$\beta = \beta_L(\cos \theta - 1) \left[\frac{R}{R+1} e^{r_2 t} + \frac{1}{R+1} e^{r_3 t} \right] + \beta_L \quad (31)$$

with

$$R = \frac{\text{tr}(\mathcal{H}_E^2) + \text{tr}(\mathcal{H}_N^2)}{\text{tr}(\mathcal{H}_Z^2)} \quad (32)$$

This equation is obtained assuming the condition $W_{NE} \gg (W_{ZE}, W_{ZN}) \gg (W_{NL}, W_{EL})$ which is valid when we are at sufficiently low temperature to have a tighter coupling between the Zeeman and exchange baths than between these baths and the lattice, and at sufficiently high field to have the exchange baths in closer contact with one another than with the Zeeman system. Under these assumptions, this kind of experiment never yields the value of the fast relaxation rate W_{NE} . The two characteristic rates which appear in the exponentials are due on one hand to the Zeeman exchange relaxation and on the other hand to the exchange lattice relaxation. Both the relaxation rates and the coefficients of the exponentials are the same as those of the "three bath model" if one regroups the normal and enhanced exchange baths. Equation (31) is also valid in the frame of GZ theory, using $R = (C_{ex} + C_4/C_Z)$, where C_{ex} and C_Z are the heat capacities of the exchange and Zeeman baths, respectively.

As for the pulse-train experiments, under the same conditions, i.e., $W_{NE} \gg (W_{ZE}, W_{ZN}) \gg (W_{NL}, W_{EL})$, the magnetization varies according to a combination of three terms, each to the power n , n being the number of pulses of angle θ . Denoting by τ the time interval between the pulses, the first term is $e^{r_1 \tau}$ due to the fast relaxation, but it does not exist if we start from equilibrium (in the same way as it does not exist in the two-pulse experiments), we then get two terms to the power n : the first one is due to the slow exchange-lattice relaxation and the second one to the Zeeman exchange. This last term appears to be significant only when θ is different from 90 degrees.

3.2. Relaxation by Atomic Diffusion

Three processes contribute to the exchange lattice relaxation¹⁰; (1) a single-phonon process whose temperature dependence is linear; (2) a two-phonon process whose temperature dependence is T^n with $n = 7$ for pure solid ^3He ^{10,12} and (3) atomic diffusion. Let us first consider the contribution of diffusion to exchange-lattice relaxation.

According to Ref. 10 this contribution can be written for a bcc lattice in the form

$$W_D = \frac{84}{a^2} D_0 \exp(-W/T) \quad (33)$$

a being the nearest neighbors distance in the solid. We use the values of W of Refs. 24 and 25 which are in good agreement with one another. D_0 is not so directly known as W . In order to obtain an upper limit of the relaxation rate due to the diffusion at low temperature, we can consider that, at the temperature where the long relaxation time appears in our experiments, the whole exchange-lattice relaxation is due to the diffusion

$$W_{ZE} + W_{ZN} \simeq W_D \frac{\text{tr} \{ \mathcal{H}_{\text{ex}}^2 \}}{\text{tr} \{ \mathcal{H}_{\text{ex}}^2 \} + \text{tr} \{ \mathcal{H}_Z^2 \}} \simeq W_D \frac{R}{R+1} \quad (34)$$

We then obtain an upper limit for D_0 taking in the previous equation the value of R for pure ^3He . For $V = 20.06 \text{ cm}^3$, $W_D(R/R+1) \leq 34 \text{ sec}^{-1}$ for $1/T = 1.5 \text{ K}^{-1}$ gives $D_0 \leq 9 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ in agreement with Ref. 24. For $V = 21 \text{ cm}^3$, $W_D(R/R+1) \leq 33 \text{ sec}^{-1}$ for $1/T = 1.9 \text{ K}^{-1}$ gives $D_0 \leq 20 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$, a value which disagrees with the one of Ref. 25.

The problem remains to explain why our upper limit of D_0 , as well as those of Ref. 24 are so much smaller than the determinations of D_0 deduced in Ref. 25 from direct Zeeman lattice relaxation times obtained at higher temperatures which should give the same information. We quote here the results of Ref. 25:

$V, \text{ cm}^3 \text{ mole}^{-1}$	$D_0 (\text{cm}^2 \text{ sec}^{-1})$ $\times 10^{-5}$
21.70	$2.7 \pm 60\%$
21.10	$4.8 \pm 70\%$
20.12	4.3
19.75	$7 \pm 40\%$

We give in Table I the values of the expected $(W_D)_{\text{max}}$ for several temperatures.

TABLE I
Maximum Relaxation Rate due to Exchange Modulation by Atomic Diffusion as a Function of Temperature

$T, \text{ K}$	1	0.8	0.6	0.5	0.4	0.3
$(W_D)_{\text{max}}, \text{ sec}^{-1}$ at $V = 20.06 \text{ cm}^3$ $W = 13.5 \text{ K}$ $D_0 = 9 \times 10^{-7} \text{ cm}^2$ sec^{-1}	8.4×10^4	29×10^3	10	12×10^{-2}	14×10^{-5}	19×10^{-10}
$(W_D)_{\text{max}}, \text{ sec}^{-1}$ at $V = 21.00 \text{ cm}^3$ $W = 11.5 \text{ K}$ $D_0 = 20 \times 10^{-7} \text{ cm}^2$ sec^{-1}	1.3×10^6	7.6×10^4	6.3×10^2	14	4.3×10^{-2}	3.3×10^{-6}

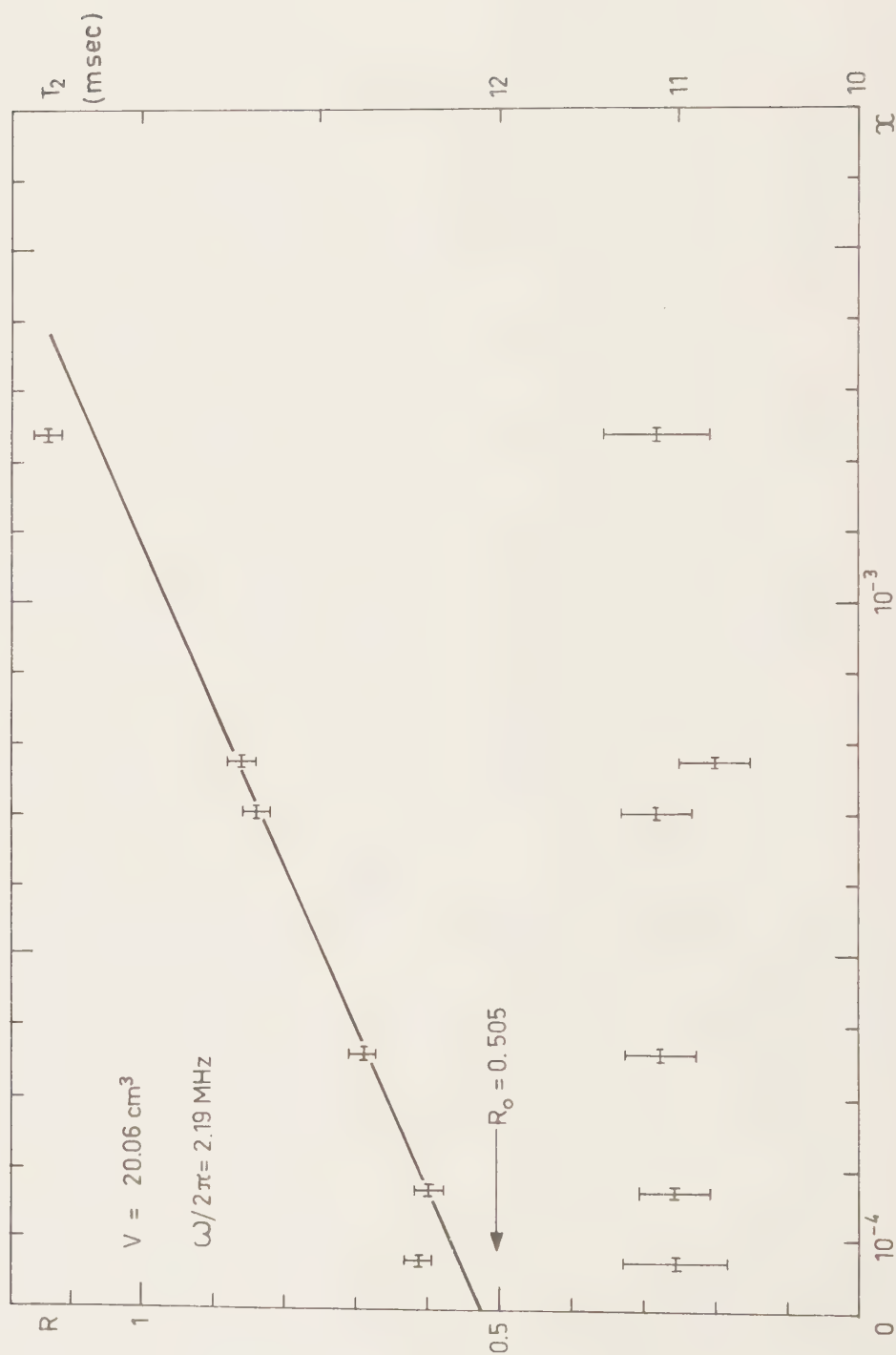


Fig. 1. The ratio $R = C_v / C_2$ of heat capacities and the transverse relaxation time at molar volume 20.06 cm^3 as a function of the ^3He concentration in the sample. The six points in the lower part of the figure are the T_2 measurements.

It turns out that, at low temperature, the exchange-lattice relaxation rate due to atomic diffusion becomes rapidly negligible compared to the relaxation rate due to the Raman process, the temperature dependences being respectively $\exp(-W/T)$ and $T^{n_{8,12,26}}$

4. RESULTS AND DISCUSSION

We have performed experiments in both phases, but we have studied mainly the bcc phase by measuring systematically T_1 , T_2 , and R at various temperatures as functions of x for two molar volumes. We analyze the data according to the models mentioned above.

4.1. The bcc Phase

4.1.1. The Heat-Capacities Ratio (Ref. 1)

We assume that W_{NE} or τ_{34}^{-1} is the larger of the relaxation rates. We thus define a unique exchange heat capacity and the ratio R of this heat capacity to that of the Zeeman bath. For the bcc lattice, we carry out the lattice sums in the first-model assumption. This yields the results:

$$R = \frac{\text{tr} \{ \mathcal{H}_{\text{ex}}^2 \}}{\text{tr} \{ \mathcal{H}_Z^2 \}} = R_0 \left\{ 1 + 14x \left(\frac{J_E}{J} \right)^2 - 15x \right\} \quad (35)$$

where

$$R_0 = 3(J/\omega)^2 \quad (36)$$

is the R value for pure ^3He . We recall that $\mathcal{H}_{\text{ex}}$ contains all exchange interactions in the system [Eq. (1)]. R is deduced from two pulse experiments using Eq. (31). We check every time that $1 - (\beta/\beta_L)$ is the sum of two exponentials, and we deduce the heat capacity ratio from the coefficient in front of the slower exponential $\exp(r_3 t)$. The results are summarized in Fig. 1. For $V = 20.06 \text{ cm}^3$ and $x \leq 2 \times 10^{-3}$, the x dependence of R is linear within experimental error: $R = R_0(1 + 825x)$. For $V = 21.00 \text{ cm}^3$ and $x \leq 2 \times 10^{-3}$, R remains constant (Table II).

4.1.2. Transverse Relaxation

Figure 1 and Table II give the results for both molar volumes we studied. For $x \leq 2 \times 10^{-3}$, T_2 is constant ($T_2 \simeq 11 \text{ msec}$ for $V = 20.06 \text{ cm}^3$ and $T_2 \simeq 22 \text{ msec}$ for $V = 21.00 \text{ cm}^3$). In our case, the magnetic field is not high enough to measure a purely adiabatic transverse relaxation time.

Case I: $V = 20.06 \text{ cm}^3$. We deduce a value for the exchange interaction by making use of a procedure explained in Ref. 27 which takes into account the detailed behavior of the field dependence of spectral densities studied in Ref. 27 and 28.

This yields $J/2\pi = 0.9 \text{ MHz}$, in fair agreement with Ref. 24. We then calculate R_0 by (40): $R_0 = 0.505$, practically the experimental limit of R for small x .

(1) From (35) we obtain the enhanced exchange J_E in our first model, $J_E/2\pi = 6.96 \text{ MHz}$. If we use this J_E value and crudely guess the ratios of characteristic

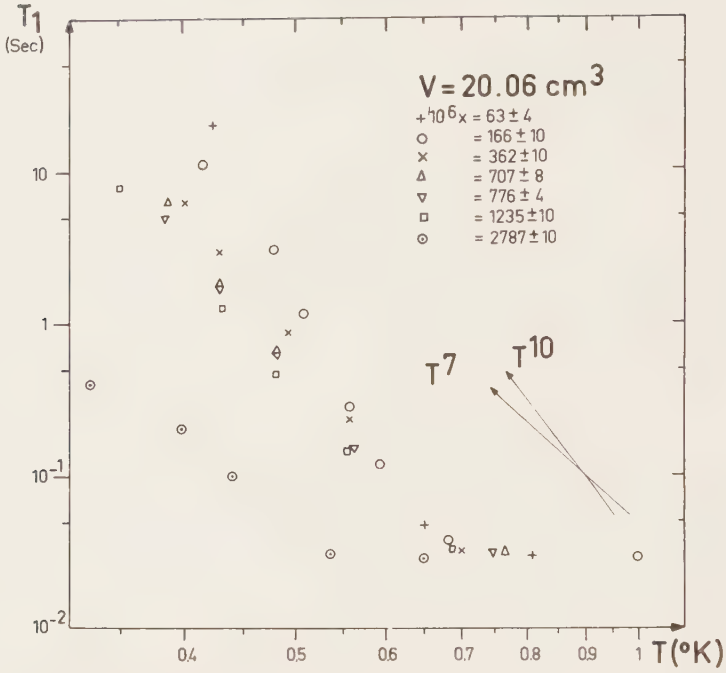


Fig. 2. The observed spin-lattice relaxation time T_1 versus lattice temperature at $V = 20.06 \text{ cm}^3$ for several ^4He impurities concentrations.

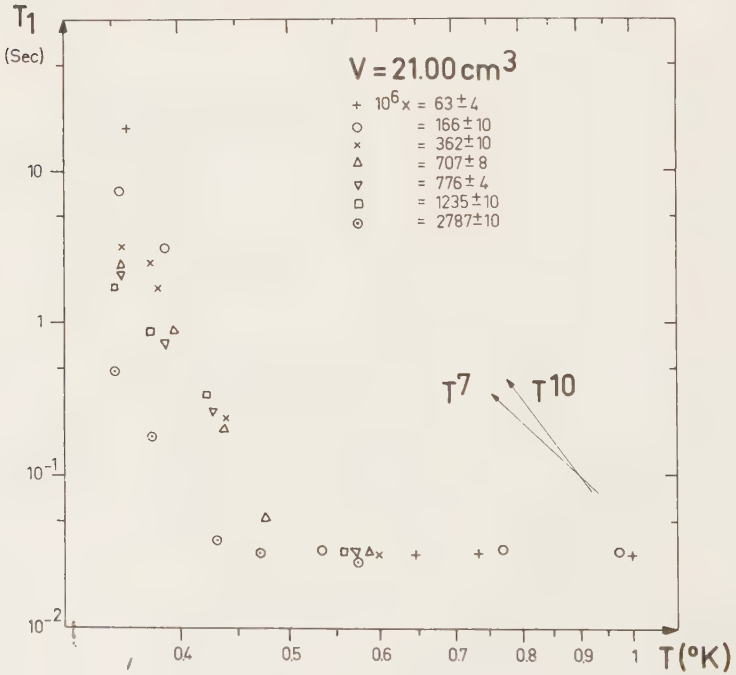


Fig. 3. The observed spin-lattice relaxation time T_1 versus lattice temperature at $V = 21.00 \text{ cm}^3$ for several ^4He impurities concentrations.

TABLE II

Values of T_2 and (C_{ex}/C_Z) Obtained for $V = 21 \text{ cm}^3$ and a Frequency $(\omega/2\pi) = 2.19 \text{ MHz}$

$x \times 10^6$	63 ± 4	166 ± 10	362 ± 10		707 ± 8		776 ± 4	1235 ± 10	2787 ± 10
T_2, msec	22.72 ± 0.2	22.68 ± 0.2	21.81 ± 0.2	22.09 ± 0.2	21.88 ± 0.2	21.45 ± 0.2	22.28 ± 0.3	19.85 ± 0.2	21.22 ± 0.4
C_{ex}/C_Z	5.4	4.1	4.2	4.5	—	4.2	4.4	3.5	11

frequencies introduced in (11):

$$\frac{\omega_N}{\omega_E} \sim \frac{J}{J_E}, \quad \frac{\omega_N}{\omega_P} \sim \frac{2J}{J + J_E}$$

we obtain a concentration dependence for T'_2 given by:

$$T'_2 = (T'_2)_{\text{pure}}[1 + 42.6x] \quad (37)$$

which is too weak to be observed.

Let us mention that J_E would be the exchange in pure ^3He for a lattice spacing larger than ours by 4%. This lattice expansion can be compared with the value of 4.7% deduced from thermal-conductivity measurements in bcc ^3He for $V = 20.2 \text{ cm}^3 \text{ mole}^{-1}$.²¹

(2) From GZ theory it appears at once that we have the same excess of specific heat and we can deduce J' from (19). We get $J'/2\pi = 0.47 \text{ MHz}$, which is of the order of J as assumed in Ref. 5.

Case II. For $V = 21.00 \text{ cm}^3$ the same calculation yields $J/2\pi = 2.38 \text{ MHz}$ in agreement with Ref. 4 and $R_0 = 3.56$, a value in fair agreement with the experimental ones whose error flags are larger than for $V = 20.06 \text{ cm}^3$. In this case, we cannot estimate either J_E or J' .

Case III. For $x = 2.8 \times 10^{-3}$ we observe no more linear dependence of either R or T_2 with x . This is qualitatively accounted for by comparing the average distance λ between ^4He atoms in a random distribution equal to $3.6a$, and the "range of enhancement" $2a$ in our first model. At this concentration, there are no more ^3He atoms unaffected by the presence of ^4He in the solid. Generally speaking this model is not expected to be good when $\lambda \leq 4a$.

4.1.3. 'Spin-Lattice Relaxation

Figures 2 and 3 summarize the results of T_1 for $V = 20.06 \text{ cm}^3$ and $V = 21.00 \text{ cm}^3$, respectively. We notice that, at relatively high temperature (0.7 K), T_1 is constant when x increases in our range of concentration. This can be explained with either model.

(1) In the frame of the first model, at this temperature, we measure $(W_{ZE} + W_{ZN})$. According to (8)

$$W_{ZE} + W_{ZN} = \int_0^\infty d\tau \frac{\text{tr} \{ [\mathcal{H}_Z, \mathcal{H}_d] U(-\tau) [\mathcal{H}_d, \mathcal{H}_Z] U(\tau) \}}{\text{tr} \{ \mathcal{H}_Z^2 \}} \quad (38)$$

In this form, the calculation is very similar to that of T_2 and we then expect only a slight dependence of T_1 on x as observed.

(2) In GZ theory we always measure W_{ZN} , for there is no direct Zeeman ^4He bath relaxation, and thus T_1 is constant with x .

We now take the data at low enough temperature and describe the long relaxation time T_1 due to the phonons by a temperature single-power law. We deduce the exponent giving the best fit: we have 10 ± 1 for $V = 20.06 \text{ cm}^3$ and $V = 21 \text{ cm}^3$. These exponents remain approximately constant within experimental errors up to $x = 1.2 \times 10^{-3}$ for both molar volumes, and are close to the exponents of Ref. 24 at lower x .

4.1.4. The x -Dependence of the Slow Relaxation Rate

We plot $1/T_1$ versus x at constant temperature such that the relaxation by diffusion processes would be negligible. We choose:

$$T = 0.423 \text{ K} \quad \text{for} \quad V = 20.06 \text{ cm}^3 \text{ (Fig. 4)}$$

$$T = 0.357 \text{ K} \quad \text{for} \quad V = 21.00 \text{ cm}^3 \text{ (Fig. 5)}$$

We then fit the curves with an equation such as (30) or (20). This yields:

$$V = 20.06 \text{ cm}^3: \frac{1}{T_1} = \frac{2.1x}{x + 2560 \times 10^{-6}} (\text{sec}^{-1}) \quad (39)$$

$$V = 21.00 \text{ cm}^3: \frac{1}{T_1} = \frac{1.98x + 4.4 \times 10^{-6}}{x + 2140 \times 10^{-6}} (\text{sec}^{-1}) \quad (40)$$

The constant term in the numerator of the second equation is not significant to the accuracy of the experiments.

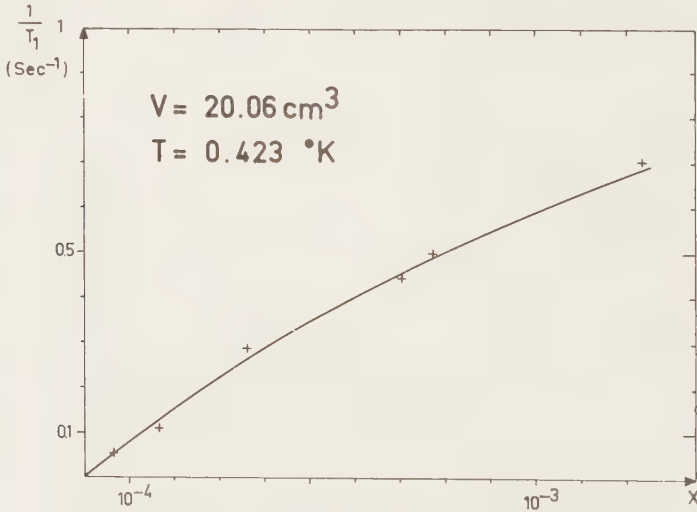


Fig. 4. The relaxation rate $1/T_1$ at $V = 20.06 \text{ cm}^3$, $T = 0.423 \text{ K}$ versus ^4He concentration x in the sample. The solid line is the best fit to experimental points: $1/T_1 = [2.1x/(x + 2560 \times 10^{-6})] (\text{sec}^{-1})$.

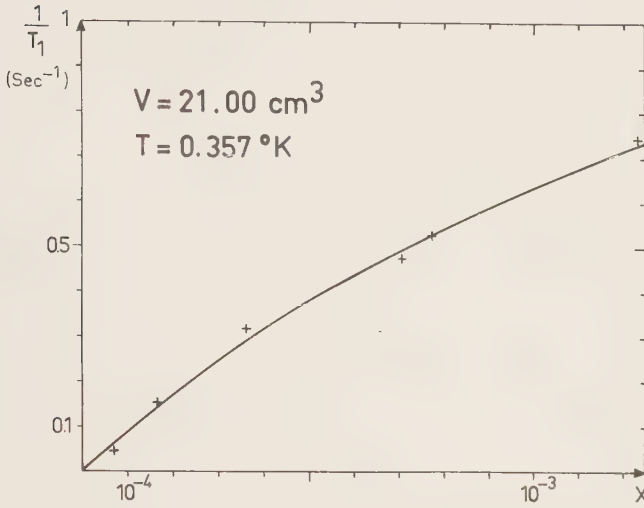


Fig. 5. The relaxation rate $1/T_1$ at $V = 21.00 \text{ cm}^3$, $T = 0.357 \text{ K}$ versus ^4He concentration x in the sample. The solid line is the best fit to experimental points: $1/T_1 = [(1.98x + 4.4 \times 10^{-6})/(x + 2140 \times 10^{-6})]$ (sec^{-1}).

Case I: $V = 20.06 \text{ cm}^3$.

(1) From (39) we deduce a rough value of W_{EL} by identification with (30). $W_{\text{EL}} \sim 2.1 \text{ sec}^{-1}$. W_{NL} can theoretically be obtained from T_1 measurements but, in our range of concentration, we cannot get it with any reasonable precision. This quantity was obtained by R. P. Giffard and J. Hatton²⁴ from measurements at lower x : $W_{\text{NL}} = 4 \times 10^{-3} \text{ sec}^{-1}$ at $T = 0.425 \text{ K}$ for $V = 19.97 \text{ cm}^3$. It is worth noting that our results are in fair agreement with Ref. 24 according to the large variation of T_1 with molar volume at low concentration as reported there. On the other hand the constant term 2.56×10^{-3} in the denominator of (39) can be compared with the result of a calculation based on the values of J and J_E , deduced from our measurements of T_2 and R , respectively, making use of (30). Such a calculation leads to a value 3.52×10^{-3} . We emphasize that this term depends only on the number of modified bonds.

(2) Using GZ theory we deduce the x dependence of T_1 from (20). We get

$$\frac{1}{T_1} = 1.8 \frac{x}{x + 3.5 \times 10^{-3}} \quad (41)$$

in good agreement with the experiment. It is worth noting that the x dependence of T_1 (out of the factor $1/T_1^0$ or W_{EL} , since we neglect W_{NL}) is always the same in the two models, for it is a ratio of heat capacities and the values of J_E and J' we use there are both deduced from the excess of the heat capacity of the exchange bath.

Case II: $V = 21.00 \text{ cm}^3$.

(1) Our R measurements are not precise enough in this case to give us a value of J_E ; we then evaluate J_E from the above expression (40), combined with (30). Using J deduced from T_2 measurements, we obtain $J_E/2\pi \simeq 16 \text{ MHz}$ which corresponds

to an increase of the exchange constant by a factor 6.7, compared with 7.7 for $V = 20.06 \text{ cm}^3$. W_{EL} is found to be 1.9 sec^{-1} .

(2) As in the preceding case, in the GZ model we use (40) to obtain an experimental value of J' by combining (40) and (20). This yields:

$$\frac{J'}{2\pi} \sim 1 \text{ MHz} \quad (42)$$

Moreover, (21) gives $1/T_1^0 \sim 1 \text{ sec}^{-1}$, of the order of the experimental measurements.

4.1.5. Other Results

We deduce J for some other molar volumes in the bcc phase from T_2 measurements. According to the preceding derivations, T_2 is approximately constant with x provided the concentration is less than 10^{-3} . The results are given in Table III.

TABLE III
Transverse Relaxation-Time Measurements at Low Temperature for Several Molar Volumes in Both bcc and hcp Phases and Values of $J/2\pi$ Deduced from These Measurements^a

Phase	V, cm^3	T_2, msec	$J/2\pi, \text{MHz}$	$R_0, \omega/2\pi = 2.19 \text{ MHz}$
<i>This work:</i>				
bcc	21.77	36	4.3	11.6
	21.15	26.5	3.1	5.98
	21.00	22	2.4	3.56
	20.87	18	1.8	2.08
	20.06	11	0.9	0.505
hcp	19.33	6.3	0.24	0.054
	19.25	5.7	0.22	0.045
	19.14	4.55	0.17	0.027
<i>Other authors:</i>				
bcc	23.1		12.9 ± 1.7	[17]
	22.50		8.84	[35]
	22.05		4.3 ± 0.6	[4]
	22.00		5.7	[35]
	22.0		4.9 ± 1.7	[17]
	21.63		4.0	[35]
	21.05		2.9 ± 0.4	[4]
	21.02		2.4	[35]
	21.0		4.62 ± 2.9	[17]
	20.6		1.8 ± 0.1	[4]
	20.04		0.94	[8]
	20.00		1.21 ± 0.1	[4]
	19.97		0.97	[24]
hcp	19.55		0.32	[8]
	19.50		0.267	[8]
	19.32		$\begin{cases} 0.205 \\ 0.33 \pm 0.02 \end{cases}$	$\begin{cases} [2] \\ [4] \end{cases}$
	18.78		0.15	[2]

^aWe quote in the lower part of the table other determinations of $J/2\pi$ by NMR, susceptibility measurements¹⁷ and exchange contribution to the pressure at low temperature.³⁵

They are in good agreement with data already published, which we quote in the table.

4.2. The hcp Phase

We have no systematic measurements as in the bcc phase. Nevertheless, we measure T_1 and T_2 versus $1/T$ for three ^4He concentrations at $V = 19.25 \text{ cm}^3$ (Fig. 6). The curves show the same kind of variation as in the bcc phase and T_1 also decreases as x increases at low x concentration. Some experiments made at high impurity concentration, $x = 8.7 \times 10^{-3}$, show that T_1 increases again at low temperature when x becomes large.²⁹ The results are given in Fig. 6. In this temperature range, we assume, as in the bcc phase, that the exchange-lattice relaxation is due to a phonon process and we deduce the exponent of a single-power law which gives the best fit for the experimental results. We thus obtain an exponent equal to 7 for all the concentrations studied in this work.

As in the bcc phase, we deduce J from T_2 measurements for several molar volumes. The results are given in Table III. We also measure the activation energy

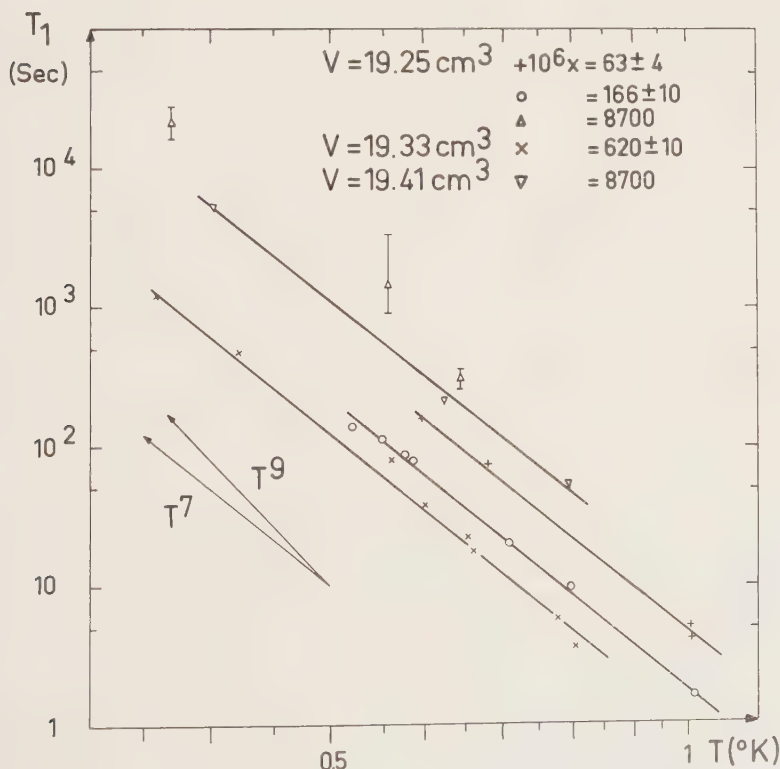


Fig. 6. Spin-lattice relaxation time T_1 in the hcp phase versus lattice temperature at three molar volumes for several ^4He concentrations.

W for the diffusion process at high temperature (between 2 and 3 K) for $V = 18.48 \text{ cm}^3$. We get $W_0 = 37.3 \text{ K}$, in good agreement with the value $W = 38.0 \pm 1 \text{ K}$ at $V = 18.52 \text{ cm}^3$ of Ref. 25. We deduce D_0 from absolute T_1 value at known temperature. According to Ref. 11 the spin-lattice relaxation time T_1 for isotropic lattice diffusion is

$$\frac{1}{T_1} = \frac{3}{2} \gamma^4 \hbar^2 I(I+1) [S_1(\omega) + S_2(2\omega)] \quad (43)$$

where $S_2(\omega) = 4S_1(\omega)$. $S_1(\omega)$ and $S_2(\omega)$ are spectral densities for the modulation of the dipolar field by translational diffusion. In the low temperature limit ($\omega\tau \gg 1$) these spectral densities can be calculated exactly^{30,31} with the result

$$S_1(\omega) = \frac{8\pi n\tau}{15k^3 a^3} \left(\frac{1}{\omega^2 \tau^2} \right) \left(1 - \frac{1}{12k^2} \right) \frac{1}{k} \quad (44)$$

The parameter k is defined by :

$$k^3 = \frac{4}{3} \frac{\pi n a^{-3}}{c \sum_k R_{jk}^{-6}} \quad (45)$$

In these expressions, a is the single jump distance of the isotropic diffusion, n is the spin density, c is the ratio of the number of nuclei to the number of lattice sites, τ is the mean time between flights.

Remembering that the second moment for a powder is

$$M_2 = \frac{3}{5} \gamma^4 \hbar^2 I(I+1) \sum_i R_{ij}^{-6} \quad (46)$$

and that c is very close to unity, T_1 can be expressed by the following equation :

$$\frac{1}{T_1} = 2M_2 \left(1 - \frac{1}{12k^2} \right) \frac{1}{k} \frac{1}{\omega^2 \tau} (\omega\tau \gg 1) \quad (47)$$

with $D = a^2/6\tau$, $D = D_0 \exp(-W/T)$. In our experiments, $T_1 = 2.53 \text{ sec}$ at $T = 2.297 \text{ K}$, and $k = 0.7428$. We deduce $D_0 = 1.15 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$. At melting temperature, $T_m = 3.400 \text{ K}$, this gives a diffusion coefficient $D = 2 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$.

Recent experiments by W. N. Yu and H. A. Reich³² in the hcp phase show two long relaxation times at low temperature, called T_3 and T_4 in their paper. T_3 does not vary with x and is always equal to the exchange-lattice relaxation time for pure ^3He ; T_4 does vary with x . At 0.53 K we can describe the concentration dependence of the T_4 results given in Fig. 3 of Ref. 32 by the expression $T_4^{-1} = 0.03 + 650x$, for $x < 1200 \times 10^{-6}$.

(1) By comparing this expression with Eq. (30) of the first model, assuming that $(W_{\text{NE}}, W_{\text{EL}}, W_{\text{NL}}) \ll (W_{\text{ZE}}, W_{\text{ZN}})$, and calculating the heat capacities of the different baths in the hcp phase with a model analogous to the one we used for the bcc phase in the limit of small x , we obtain a unique value for J_E . Using the data of Ref. 32 we get $W_{\text{EL}}(J_E/2\pi)^2 \simeq 82$, with W_{EL} expressed in sec^{-1} and $J_E/2\pi$ in MHz.

(2) An extension of the mass-fluctuation wave theory to the hcp lattice provides a concentration dependence for T_4^{-1} of the same order of magnitude as the experimental results. A rough calculation gives $T_4^{-1} \sim 2 \times 10^2 x$ for small x .

It should be mentioned that neither the enhanced exchange nor the mass fluctuation can provide an explanation of the T_3 relaxation time which subsists even for impure solid ^3He .

5. CONCLUSION

Although our first model gives a coherent explanation of the NMR experiments in solid ^3He containing ^4He impurities, several criticisms may arise about the interpretation. The first concerns the existence of such enhanced exchange which has not been found by microscopic calculations. The others are more directly related to the model if we assume the existence of J_E .

(1) We attribute a unique J_E value to every bond around a ^4He atom, which is certainly a rough approximation because the distance between ^3He atoms around a ^4He impurity is not increased for all ^3He pairs.

(2) Moreover, for the sake of simplicity, J_E and J are supposed to exist only for nearest neighbors. This could introduce significant errors in presence of distortion. Let us call a the nearest-neighbor distance in pure ^3He and assume that, in the bcc phase, only the first shell of ^3He atoms around a ^4He is displaced towards the ^4He atom by δa with respect to their positions in pure ^3He . In such a case, some of the bonds we have characterized by J_E have a length $a + \delta a$ while two ^3He atoms both first neighbors of ^4He and second neighbors with respect to one another are separated by a distance $(2/\sqrt{3})(a - \delta a)$. These two bonds are equal for $\delta a/a \sim 7\%$, where we found that J_E in our samples would correspond to a pure ^3He lattice whose parameter is increased by 4%. It seems then useful to include in microscopic calculations next-nearest-neighbors exchange interactions whose influence is even less negligible than for pure ^3He .

As for the GZ model, it gives a fairly good explanation of the experimental results without including this enhanced exchange which we cannot prove to exist, and thus it seems to be more satisfactory than the first one. However, the range of validity of this description has to be deeply investigated by a careful study of the lifetime of the mass fluctuation waves due to the interactions with phonons.

We emphasize that these two models are characterized by three relaxation times depending on the relative values of the characteristic relaxation rates between the baths. Both W_{NE} and τ_{34}^{-1} have been found to be proportional to the concentration of ^4He and to the characteristic frequency of the energy bath due to the impurities. At the present time, we can see no experiment which could be explained with only one of these models and would then enable us to make a definite choice on experimental grounds.

Our current experiments aim to verify the frequency variation of R and to get more precise results for $V = 21.00 \text{ cm}^3$ to confirm the expected x dependence of R .

Varma recently made another attempt^{3,3} to explain the properties of bcc ^3He . He considers the four-spin exchange Hamiltonian obtained by calculating the

indirect interaction between two pairs of first-neighbor spins due to the virtually emitted and absorbed phonons in the exchange of spins inside each pair. By this way he explains the low temperature θ_D anomaly in bcc ^3He without being entirely convincing.^{34*}

APPENDIX I. ^4He CONCENTRATION DEPENDENCE OF W_{NE}

Let us consider Eq. (7) which gives W_{NE} . We can write $\mathcal{H}_P$ as the sum of two terms:

$$\mathcal{H}_P = \mathcal{H}_d + \mathcal{H}'_N \# \mathcal{H}'_N$$

The numerator of (7) can thus be written in the form of lattice sums:

$$\begin{aligned} \int_0^\infty d\tau \operatorname{tr} \left\{ \left[\sum_{i < j} J \mathbf{I}_i \cdot \mathbf{I}_j, \sum_{\alpha'} \sum_{\substack{k,l \\ \in \alpha'}} J \mathbf{I}_k \cdot \mathbf{I}_l \right] U(-\tau) \right. \\ \left. \times \left[\sum_{\beta} \sum_{\substack{m,n \\ \in \beta}} J_E \mathbf{I}_m \cdot \mathbf{I}_n, \sum_{\gamma'} \sum_{\substack{p,q \\ \in \gamma'}} J_N \mathbf{I}_p \cdot \mathbf{I}_q \right] U(\tau) \right\} \end{aligned} \quad (\text{I.1})$$

where α, β, γ are indices labelling ^4He impurities. Using these indices bare means that we consider the enhanced exchange bonds around the corresponding ^4He , and priming them means that we consider the perturbation bonds. Let us write $U(\tau)$ in Eq. (I.1) as a function of lattice sums.

$$U(\tau) = \exp \{ i(\mathcal{H}_Z + \mathcal{H}_E + \mathcal{H}_N)\tau \}$$

Thus we have:

$$\begin{aligned} \int_0^\infty d\tau \operatorname{tr} \left\{ \sum_{\alpha'} \sum_{\alpha''} \left[\sum_{\substack{i < j \\ \in \alpha'}} J \mathbf{I}_i \cdot \mathbf{I}_j, \sum_{\substack{k,l \\ \in \alpha'}} J \mathbf{I}_k \cdot \mathbf{I}_l \right] \times \sum_{\beta} \sum_{\beta'} \sum_{\beta''} \left[\sum_{\substack{m,n \\ \in \beta}} J_E \mathbf{I}_m \cdot \mathbf{I}_n, \right. \right. \\ \left. \times \exp \left\{ -i \left(\sum_{\substack{r,s \\ \in \beta}} J_E \mathbf{I}_r \cdot \mathbf{I}_s + \sum_{\substack{t,u \\ \in \beta''}} J \mathbf{I}_t \cdot \mathbf{I}_u \right) \tau \right\} \sum_{\substack{p,q \\ \in \beta'}} J \mathbf{I}_p \cdot \mathbf{I}_q \right. \\ \left. \left. \times \exp \left\{ +i \left(\sum_{\substack{v,w \\ \in \beta}} J_E \mathbf{I}_v \cdot \mathbf{I}_w + \sum_{\substack{x,y \\ \in \beta''}} J \mathbf{I}_x \cdot \mathbf{I}_y \right) \tau \right\} \right] \right\} \end{aligned} \quad (\text{I.2})$$

where α'', β'' characterize those $\mathcal{H}_N$ bonds which are coupled to $\mathcal{H}'_N$ around α, β impurities. The first commutator in Eq. (I.1) does not cancel only if the two sums are related to the same impurity α . In the same way, the second commutator is non-zero only if $\gamma = \beta$. Then we get only the β indices in the exponentials when we

* A second-order perturbation theory gives a four-particle spin exchange Hamiltonian noted $H_{is} = \frac{1}{2} \sum_{ij, mn} [H_{ij, mn}^{(1)} + H_{ij, mn}^{(2)} + \dots]$. Varma uses the part $H_{ij, mn}^{(2)}$ to explain the low-temperature θ_D anomaly in bcc ^3He with a four-particle exchange larger than the two-particle exchange, surprisingly enough. Moreover, difficulties appear with the part $H_{ij, mn}^{(1)}$ of the spin Hamiltonian: to calculate the partition function of the system including this new contribution, we need to evaluate terms such as: $\operatorname{tr} \{ H_{is} \mathcal{H}_{ex}^2 \}$. The summation over the whole crystal of such terms gives a nonconvergent integral, depending on the shape of the solid, due to the long range of $H_{ij, mn}^{(1)}$.

include them in the second commutator. The trace thus bears only on two indices. If the impurities are diluted in such a way that there are no common bonds between α'' and β'' and if α and β characterize two different ^4He impurities, the trace does not cancel only if $\alpha = \beta$. Since $\text{tr} \{ \mathcal{H}_N^2 \}$ is the sum of two terms, the first one constant and the second one proportional to x , W_{NE} is proportional to x in the limit of small ^4He concentrations.

The same derivation can be applied to W_{ZE} .

APPENDIX II. T_2 CALCULATION FOR A bcc LATTICE

If the sample is assumed to be a powder, the function $G_\omega(\tau)$ in Eq. (10) can be written as

$$G_\omega(\tau) = \frac{9}{10} \hbar^2 \gamma^4 \sum_{i < j} R_{ij}^{-6} \frac{\text{tr} \{ A_1^{ij} \exp \{ i(\mathcal{H}_N + \mathcal{H}_E)\tau \} A_{-1}^{ij} \exp \{ -i(\mathcal{H}_N + \mathcal{H}_E)\tau \} \}}{\text{tr} \{ I_z^2 \}} \quad (\text{II.1})$$

R_{ij} is the distance between lattice sites i and j and:

$$A_{\pm 1}^{ij} = I_{\pm}^i I_z^j + I_{\mp}^j I_z^i$$

Since $\mathcal{H}_N$ and $\mathcal{H}_E$ commute, we divide the lattice sum in three parts: this yields

$$G_\omega(\tau) = G_E(0) f_E(\tau) + G_N(0) f_N(\tau) + G_P(0) f_P(\tau) \quad (\text{II.2})$$

Let us evaluate the three lattice sums occurring in $G_\omega(\tau)$ as functions of M_2 , the second moment for pure ^3He :

$$G_a(0) = \frac{9}{10} \hbar^2 \gamma^4 \sum_{\substack{i < j \\ \in a}} \frac{\text{tr} \{ A_1^{ij} A_{-1}^{ij} \}}{R_{ij}^6 \text{tr} \{ I_z^2 \}} \quad (\text{II.3})$$

the index a standing for N , E , or P .

This expression gives M_2 when the sum is extended to the whole lattice. $G_a(0)$ is thus proportional to M_2 with a coefficient equal to the ratio of the number of bonds included in a to the total number of bonds. Let us recall that for a bcc lattice: $\sum_i (1/R_{ij}^6) = 12.252/a^6$, a being the lattice nearest-neighbor distance.

Let us calculate the number of bonds included in E : each ^4He has eight nearest neighbors ^3He atoms A each of which has seven ^3He atoms B nearest neighbors, none of them being of the A kind. We thus have 56 such bonds per ^4He atom and the sum gives $56Nx$, N being the total number of He atoms. The total number of bonds being $N/2$, the coefficient of M_2 in the summation becomes: 9.13x.

We now evaluate the number of bonds arising in P . The summation includes all the bonds starting from B atoms except those characterized by an exchange parameter J_E , i.e., those between B and the nearest-neighbor A atoms, as also the bonds between B and substitutional ^4He . For such a ^4He atom, the neighbors of

type B can be classified in the following way:

- 0 first neighbor at distance a
- 6 second neighbor at distance $2a/\sqrt{3}$
- 12 third neighbor at distance $2a\sqrt{\frac{2}{3}}$
- 0 fourth neighbor at distance $a\sqrt{\frac{11}{3}}$
- 8 fifth neighbor at distance $2a$

The main correction to the sum is given by

$$\sum_{\text{atoms } B} [1/(R_{ij})^6] = 3.29/a^6$$

We then obtain

$$\sum_P = (259.3/a^6)Nx$$

and the coefficient of M_2 in $G_P(0)$ is: 42.33 x .

The sum including the normal bonds is deduced by subtraction of the other contributions from the total lattice sum. The corresponding coefficient is $(1 - 53.46x)$. As for pure ^3He , let us make the Gaussian assumption for the three functions arising in Eq. (II.2). $G_\omega(\tau)$ can then be written as

$$G_\omega(\tau) = (1 - 53.46x)M_2 \exp(-\frac{1}{2}\omega_N^2\tau^2) + 9.13M_2x \times \exp(-\frac{1}{2}\omega_E^2\tau^2) + 42.33M_2x \exp(-\frac{1}{2}\omega_P^2\tau^2)$$

The Fourier transform yields:

$$\frac{1}{T_2} = \sqrt{\frac{\pi}{2}} M_2 \left[\frac{1}{\omega_N} + x \left(\frac{42.33}{\omega_P} + \frac{9.13}{\omega_E} - \frac{53.46}{\omega_N} \right) \right]$$

which is equivalent to (23).

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